Photochemistry of methyl(hydrido)diplatinum(II) complexes, including examples of C—H and C—C bond formation by intramolecular reductive elimination¹

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This paper is dedicated to Professor Paul de Mayo on the occasion of his 60th birthday

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Photolyses of the complex cations $[Pt_2H(\mu-H)Me(\mu-dppm)_2]^+$, $[Pt_2(\mu-H)Me_2(\mu-dppm)_2]^+$, and $[Pt_2Me_3(\mu-dppm)_2]^+$ lead to reductive elimination of H₂, CH₄, and C₂H₆, respectively. However, photolysis of $[Pt_2Me_3(\mu-dppm)_2]^+$ in pyridine gives $[PtMe_2(dppm)]$ and $[PtMe(C_5H_5N)(dppm)]^+$. The reductive eliminations of CH₄ and C₂H₆ are shown to be primarily intra-molecular reactions by isotopic labelling. Quantum yields are reported and the mechanisms of reaction discussed.

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Les photolyses des complexes cationiques $[Pt_2H(\mu-H)Me(\mu-dppm)_2]^+$, $[Pt_2(\mu-H)Me_2(\mu-dppm)_2]^+$ et $[Pt_2Me_3(\mu-dppm)_2]^+$ conduisent respectivement à des éliminations réductrices de H₂, CH₄ et C₂H₆. Toutefois, la photolyse de $[Pt_2Me_3(\mu-dppm)_2]^+$ dans la pyridine fournit du $[PtMe_2(dppm)]$ et du $[PtMe(C_5H_5N)(dppm)]^+$. Faisant appel à des marquages isotopiques, on démontre que les éliminations réductrices de CH₄ et C₂H₆ sont principalement des réactions intramoléculaires. On rapporte les rendements quantiques et on discute des mécanismes réactionnels.

[Traduit par le journal]

Introduction

In previous papers we have reported the synthesis and reactions of the complexes ions $[Pt_2H_nMe_{3-n}(\mu-dppm)_2]^+$, n = 0-3, dppm = $Ph_2PCH_2PPh_2$, 1-4(1-6).



The thermal and photochemical reductive elimination of H_2 from complex 1 was been well studied (3, 7–13) but the properties of 2–4 have not been investigated in detail. Complex 2 undergoes reductive elimination of methane on treatment with the alkyne CF₃C=CCF₃, but hydrogen is eliminated on reaction with tertiary phosphines (5, 6). Complex 3 undergoes reductive elimination of methane on reaction with CF₃C=CCF₃, but reacts only very slowly with phosphines (4, 6), while 4 is stable to thermal reductive elimination (2). All complexes 1–4 have been shown to be photosensitive, but only for 1 has the reaction been studied in detail (reaction [1], L = C₅H₅N, MeCN, or tetrahydrofuran) (7–9).



The photochemical reactions of 2-4 are of considerable interest because, potentially, they can lead to binuclear cou-

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pling of C—H or C—C bonds and such reductive eliminations (or the reverse oxidative additions) are significant in catalysis involving formation or activation of alkanes at transition metal centres (14–20). There have been no detailed studies of photochemical reductive eliminations leading to C—H or C—C bond formation even in mononuclear systems, and there are only a few qualitative reports of such reactions (4, 14, 21–25). This article reports a study of the photochemistry of complexes 2-4, with particular emphasis on 3 and 4 which can give reductive elimination of methane and ethane, respectively. A preliminary account of parts of this work has been published (26).

Results

Photochemistry of the methyl(hydrido)diplatinum complexes 2 and 3

Photolysis of complexes 2 and 3 in pyridine or acetonitrile solution occurred according to eqs. [2] and [3], giving in each case the methyldiplatinum(I) complex.



The gaseous products, H_2 or CH_4 , were detected using gas chromatography. In reaction [3] no ethane was detected, while in reaction [2] only a trace of the alternative product methane was detected. The complexes **6***a* and **6***b* were formed without



FIG. 1. Changes in the uv-visible absorption spectrum on irradiation of 2 in MeCN, with the following numbers of Einsteins of incident light $(362 \pm 7 \text{ nm})$: (a) 0, (b) 4.0×10^{-7} , (c) 8.0×10^{-7} , (d) 14.4×10^{-7} , (e) 26.4×10^{-7} , (f) extended irradiation.

detectable impurities (¹H and ³¹P nmr spectra) of the alternative products 5a and 5b, respectively, indicating that the reactions are very selective.

Complex **6***a*, as the $[SbF_6]^-$ salt, is a yellow solid, which is stable in air at room temperature. It was characterized by elemental analysis and by the ¹H and ³¹P{¹H} nmr spectra. The spectra are very characteristic and the parameters (Experimental section) are very similar to those for other methyldiplatinum(1) complexes $[Pt_2MeL(\mu-dppm)_2]^+$, with L = tertiary phosphine, which have been discussed in detail elsewhere (5, 27). Complexes **6***b* and **6***c*, with the weakly co-ordinated MeCN or Me₂CO ligands, were not sufficiently stable to be isolated but were positively characterized by comparison of the ¹H nmr data with those for **6***a*, and by conversion to **6***a* on addition of pyridine.

Reaction [2] involving reductive elimination of H₂ is analogous to reaction [1] studied previously (7-9), but reaction [3] is of a new and significant type and so a labelling experiment was carried out to determine if reductive elimination of methane is an intramolecular or intermolecular process. A mixture of $[Pt_2(\mu-H)Me_2(\mu-dppm)_2][PF_6]$ and $[Pt_2(\mu-D)(CD_3)_2-(\mu-dppm)_2][PF_6]$ gave CH₄ and CD₄, with only traces of CH₃D or CD₃H, on photolysis. It is thus proved that intramolecular reduction elimination occurs. When photolysis was not complete, the yield of CH₄ was greater than that of CD₄. This suggests that, as in the photolysis of 1, there is a significant primary isotope effect on the rate of reaction (9).

Quantum yields for photolysis of 2 or 3 in pyridine or acetonitrile were determined by irradiation of rigorously degassed solutions in quartz cuvettes with 362 ± 7 nm light from a Jasco Spectroirradiator, previously calibrated using ferrioxalate actinometry. Typical sets of uv-visible absorption spectra obtained during irradiation of 2 and 3 are shown in Figs. 1 and 2. For photolysis of 2 good isosbestic points were observed (Fig. 1) but for photolysis of 3 there were no crossover points in the uv-visible spectra (Fig. 2). In each case, the extent of reaction was determined by monitoring the optical density at



FIG. 2. Changes in the uv-visible absorption spectrum on irradiation of **3** in MeCN, with the following numbers of Einsteins of incident light (362 ± 7 nm): (a) 0, (b) 3.6×10^{-7} , (c) 6.0×10^{-7} , (d) 8.4×10^{-7} , (e) 11.2×10^{-7} , (f) extended irradiation.

TABLE 1. Quantum yields $(362 \pm 7 \text{ nm})$ for photolysis of diplatinum complexes

Complex	Quantum yield"		
	ру	MeCN	Reference
$\frac{\left[\operatorname{Pt}_{2}\operatorname{H}_{2}(\mu-\operatorname{H})(\mu-\operatorname{dppm})_{2}\right]\left[\operatorname{PF}_{6}\right]}{\left[\operatorname{Pt}_{2}\operatorname{H}_{2}(\mu-\operatorname{H})(\mu-\operatorname{dppm})_{2}\right]\left[\operatorname{PF}_{6}\right]}$	0.57	0.81*	9
$[Pt_2H(\mu-H)Me(\mu-dppm)_2][SbF_6]$	0.21	0.37	This work
$[Pt_2(\mu-H)Me_2(\mu-dppm)_2][PF_6]$	0.30	0.34	This work
$[Pt_2Me_3(\mu-dppm)_2][PF_6]^c$	0.6	0.1	This work

"In all cases, these are Φ for photodecomposition of reagent.

"Geoffroy et al. quote $\Phi = 0.62$ for photolysis using 366 nm light (7).

 $^{\circ}\Phi = 0.6$ in C₆H₆, 1.2 ± 0.3 in acetone, 2.0 ± 0.1 in CH₂Cl₂.

suitable points, and good linear plots of quanta absorbed by 2 or 3 vs. extent of conversion were then obtained. From these data, the quantum yields were determined and their values are given in Table 1.

It can be seen from Table 1 that the quantum yields for photolysis of 1-3 are all high, with Φ for $1 > 2 \approx 3$, and the quantum yields are in all cases slightly higher in acetonitrile than in pyridine.

Photochemistry of the trimethyldiplatinum(II) complex, 4

Photolysis of complex 4 in pyridine gave no gas evolution, and monitoring by ¹H and ³¹P{¹H} nmr indicated that the products were mononuclear complexes as shown in reaction [4].

$$[4] \quad 4 \quad \xrightarrow{h\nu} \left[\begin{matrix} Me \\ Me \end{matrix} Pt \end{matrix} P \\ \begin{matrix} P \\ P \end{matrix} \right] + \left[\begin{matrix} Me \\ C_5H_5N \end{matrix} Pt \end{matrix} P \\ \end{matrix} \right]^+$$

These complexes could not be separated, but were positively identified by the ¹H and ³¹P{¹H} nmr spectra. [PtMe₂(dppm)] is a known complex and was characterized by comparison of the nmr parameters with those for an authentic sample (28, 29). A sample containing the cation [PtMe(C_5H_5N)(dppm)]⁺ was pre-

pared independently by reaction of |PtClMe(dppm)| with 1 mol-equiv. of silver nitrate followed by excess pyridine. The ¹H and ³¹P{¹H} nmr spectra, which are very characteristic (Experimental section), were identical with those of the second photolysis product of reaction [4].

Extended photolysis of the above mixture did lead to some ethane formation and an uncharacterized symmetrical diplatinum complex was also formed. The quantum yield of the primary photochemical reaction of reaction [4] was high (Table 1) but the secondary photolysis was very inefficient and has not been studied in detail.

Photolysis of **4** in acetonitrile occurred cleanly in the initial stages to give ethane and complex **6***b*, identified by its ¹H and ³¹P{¹H} nmr and uv-visible absorption spectra. However, the quantum yield was low (Table 1), and, as a result, further photolysis of product **6***b* became competitive in the later stages and the isosbestic points were lost. This reaction gave the first indication of a photochemical reductive elimination with C—C bond formation, and so the photolysis was studied in several other solvents.

Efficient reductive elimination of ethane occurred on photolysis of **4** in benzene, acetone, or dichloromethane as solvents. In benzene, the product of photolysis was very insoluble and precipitated during photolysis so that an accurate quantum yield could not be obtained. In acetone, the primary products were C_2H_6 and complex **6***c* and the stoichiometry was clean until the late stages, when photolysis of **6***c* became a problem. In this reaction 1.0 ± 0.1 mol of ethane was formed for each mol of **4** decomposed and the quantum yield (362 ± 7 nm) was 1.2 ± 0.3 . The large uncertainty in the quantum yield arose due to problems with the secondary photolysis of **6***c*. The quantum yield is within experimental error of 1.0, and is an order of magnitude greater than that in acetonitrile solvent.

In dichloromethane solution, the stoichiometry of reaction was different and only 0.5 mol of C_2H_6 was formed for each mole of 4 decomposed (reaction [5]).

$$[5] \quad 2[\operatorname{Pt}_2\operatorname{Me}_3(\mu\operatorname{-dppm})_2]^+ \xrightarrow{h\nu} 2[\operatorname{Pt}_2\operatorname{Me}_2(\mu\operatorname{-Cl})(\mu\operatorname{-dppm})_2]^+ + C_2H_d$$

The product 7 has been characterized previously (29) and was isolated in quantitative yield. It is clear that a chlorine atom abstraction from solvent dichloromethane occurs during this reaction. The quantum yield for disappearance of 4 was 2.0 ± 0.1 .

Because this clean photochemical C—C coupling reaction has no precedents, attempts were made to determine if the elimination is an intramolecular process. Photolysis of an equimolar amount of $[Pt_2Me_3(\mu-dppm)_2]|PF_6]$ and $[Pt_2(CD_3)_3-(\mu-dppm)_2]|PF_6]$ in CH₂Cl₂ or acetone gave a product ratio of C₂D₆: CH₃CD₃ of 1:0.4 and 1:1.0, respectively (C₂H₆ yields could not be determined accurately due to high background at m/e 30, under the conditions used, with analysis by mass spectrometry). An intramolecular reaction should give C₂D₆: CH₃CD₃ = 1:0, while an intermolecular coupling reaction should give a ratio of 1:2. The experiment thus proves that at least 50% of the reaction occurs by intramolecular coupling in acetone and at least 80% in dichloromethane.

An effort was made to determine which two methyl groups in **4** were eliminated. However, an attempt to synthesize the unsymmetrical labelled complex ion $[(CD_3)_2Pt(\mu-dppm)_2Pt-CH_3]^+$ by reaction of $[Pt(CD_3)_2(dppm)]$ with |PtClMe(dppm)]gave a sample of **4** in which complete scrambling of CD₃ and CH₃ groups had occurred, as determined by ¹H nmr spectroscopy. Thus it was not possible to solve this important problem. We suspect that the alkyl-for-alkyl exchange reactions which lead to this scrambling, and which have also been observed in other diplatinum complexes (30), may also account for the apparent intermolecular component of the reductive elimination reaction noted above.

Discussion

The photolyses of the family of complex cations, 1-3, in each case leads to an overall binuclear reductive elimination in which the formal oxidation state of each platinum centre decreases from +II to +I. The reactions are very selective. Thus complex 2 gives hydrogen rather than CH_4 and complex 3 gives CH₄ rather than C₂H₆, and so it can be concluded that bond formation is favoured in the sequence $H-H > CH_3-H >$ CH_3 — CH_3 in these complexes. However, it should be noted that, in 1-3, hydride occupies the bridging position and, since it is possible that the reaction always involve loss of the bridging ligand, only for 2 is there positive evidence that H-Hbond formation is preferred rather than CH₃—H bond formation. The same selectivity is observed in thermal reductive eliminations induced by tertiary phosphine ligands (4, 5, 27), but hexafluorobut-2-yne induces selective reductive elimination of methane from 2(6). In the thermal reactions, the rates of reaction follow the sequence $1 > 2 \ge 3$ (4, 13, 27), but there are only small differences in the rates of the photochemical reactions (Table 1). In particular, the quantum yields for photolysis of 2 (which gives H_2) and 3 (which gives CH_4) are very similar.

It has been proved that the reductive eliminations from 1 and 3 are intramolecular, but the detailed mechanisms of reaction cannot be determined unequivocally. For photolysis of 1, a mechanism involving reductive elimination of H₂ from a single metal centre was proposed (9), but a subsequent study of the thermal reductive elimination suggested a true binuclear reductive elimination in which hydride ligands coupled across two platinum centres (13). The results from the present study can be interpreted in terms of either mechanism (see refs. 13, 18, 30, 32-35 for related discussions of mechanisms in binuclear and cluster complexes), but the primary photochemical step in all cases is probably the cleavage of the Pt₂(μ -H) linkage by excitation of an electron to a σ^* (PtPt) orbital (9, 31).

The photochemically-induced reductive elimination of ethane from 4 appears to be a unique reaction. Photolysis of alkyl transition metal complexes usually gives homolysis of the M—C bond to give alkyl radicals (36, 37), though β -elimination, isomerization, loss of other ligands with no reaction of the M—R bond, and other reactions can also occur (22-25,38-40). Photolysis of mononuclear alkyl platinum(II) or alkylplatinum(IV) complexes leads primarily to the formation of alkyl radicals (41-43), though reductive elimination may be oberved with platina(IV)cycloalkanes (22, 23, 44, 45). There are two properties of 4 which might lead to its unique reactivity. Firstly, the primary photochemical process almost certainly will involve cleavage of the Pt-Pt bond by excitation of an electron to the $\sigma^*(PtPt)$ orbital, and this excited state is not possible with mononuclear complexes. However, it is not obvious why this excited state should cause reductive elimination from the dimethylplatinum centre (46). Secondly, since 4 is binuclear, new mechanisms, such as a coupling of methyl groups across two platinum centres, become available. The experimental data cannot distinguish between these



FIG. 3. Plot of concentration of 4 (mol L^{-1}) vs. light (362 \pm 7 nm) absorbed by 4 (E), showing that the quantum yield is independent of concentration of 4.

possibilities.

We have shown that the reductive elimination of ethane is at least partially intramolecular by a labelling experiment, and we believe that this reaction is almost entirely intramolecular. In order to give the observed quantum yields (Table 1) for an intermolecular elimination, the lifetime of the excited state would need to exceed 10^{-5} s to allow complete quenching by a second molecule of 4 (assuming $k_q \sim 10^{10}$ s⁻¹ and $\sim 99\%$ efficiency of quenching) at the concentrations used. Few lifetimes of organometallic excited states have been measured but most such lifetimes are $< 10^{-6}$ s at 298 K (47). In addition, an intermolecular process should give a concentration-dependent quantum yield which was not observed (Fig. 3).

Finally, a comment is needed on the solvent dependence of the quantum yields and reaction products. The good donor pyridine can presumably co-ordinate to the monomethylplatinum centre of 4 after photochemical cleavage of the PtPt bond, and cleavage of the dimer to mononuclear fragments (reaction [4]) follows. In the poor donor solvent acetone, the excited state gives intramolecular loss of C₂H₆ with a quantum yield of ~ 1 . The lower quantum yield in acetonitrile may be explained if this is a good enough ligand for platinum to coordinate reversibly and hence deactivate the excited state but not good enough to cause breakdown to mononuclear fragments. Finally, in dichloromethane intramolecular loss of ethane from 4 gives $[Pt_2Me(\mu-dppm)_2]^+$, which must then accept a methyl group from a second molecule of 4 in a rapid thermal reaction and abstraction of Cl radicals from CH₂Cl₂ solvent gives the observed product (reaction [5]). The true quantum yield for the reductive elimination is therefore 1.0.

Experimental

¹H and ³¹P{¹H} nmr spectra were recorded using Varian XL100 or XL200 NMR spectrometers, and chemical shifts are quoted with re-

spect to TMS or trimethylphosphate, respectively. Gas analysis (H₂, CH₄, and C₂H₆) was carried out by injection of a standard volume of gas formed in the photochemical reaction into a Varian Series 1400 gas chromatograph. Calibration was carried out by injection of known volumes of the pure gases into the reaction vessel containing only solvent, then allowing to equilibrate and sampling as above. The columns used were $6' \times 1/8''$ packed with Molecular Sieve 5A or Porapak Q.

$[Pt(CD_3)_2(dppm)]$

A solution of CD₃Li (24 mL, 1.7 *M*), freshly prepared from Li and CD₃I in ether, was added dropwise to a suspension of $|PtCl_2(dppm)|$ (1.52 g) in ether (30 mL) cooled to 0°C. The solution was allowed to warm to room temperature. After 1 h, the mixture was hydrolysed with cold saturated aqueous NH₄Cl solution (5 mL). The layers were separated, and the aqueous layer was further extracted with CH₂Cl₂. The organic extracts were dried over MgSO₄ and evaporated to yield the product (0.62 g).

$[Pt_2(CD_3)_3(\mu - dppm)_2][PF_6]$

A mixture of $[Pt(CD_3)_2(dppm)]$ (0.19 g) and $[PtCl_2(dppm)]$ (0.066 g) in methanol (15 mL) was heated under reflux for 1 h. $[NH_4][PF_6]$ (0.12 g) was then added, heating was continued for 5 min, the solution was cooled, and water was added dropwise to precipitate the product as a yellow solid. This was purified by precipitation from CH_2Cl_2 solution by slow addition of hexane, and was identified by the ¹H and ³¹P{¹H} nmr spectra (2).

$[Pt_{2}(\mu-D)(CD_{3})_{2}(\mu-dppm)_{2}]/PF_{6}]$

This was prepared by the literature method for the synthesis of **3** (4), but using $[Pt(CD_3)_3(\mu\text{-dppm})_2][PF_6]$ (0.09 g), NH₄[PF₆] (0.06 g) in CH₃OD (10 mL) with Na[BD₄] (0.1 g) in CH₃OD (3 mL). The yield was 0.06 g (70%) and the complex was characterised by the ¹H and ³¹P{¹H} nmr spectra (4).

$[Pt_2Me(C_5H_5N)(\mu - dppm)_2][SbF_6]$

A solution of $|Pt_2H(\mu-H)Me(\mu-dppm)_2||SbF_6|$ (0.05 g) in dry pyridine (20 mL) was deoxygenated by passing nitrogen through the solution for 45 min. The reaction vessel was a flat-sided Pyrex flask, with a sidearm fitted with a 1 mm quartz cuvette to allow monitoring of the reaction by uv-visible absorption spectroscopy. The solution was irradiated for 2h, using a medium pressure Hg lamp 12 cm from the sample and using a water filter, after which no further change in absorption spectrum occurred. A sample of the gas phase was analysed by gc, and showed hydrogen and a trace of methane to be present. The solvent was then removed under high vacuum to give the product as a yellow solid in quantitative yield. *Anal.* calcd. for C₅₆H₅₂-NF₆P₄Pt₂Sb: C 45.2, H 3.5; found: C 44.7, H 3.6. ¹Hmr (C₅D₅N) δ : 0.53[*m*, ²*J*(PtH) 72.5, ³*J*(PH) 11, *MePt*|, 5.29[*m*, CH₂P₂]. ³¹Pmr (C₅D₅N) δ : 8.4[*m*, ¹*J*(PtP^A) 2930], -4.7[*m*, ¹*J*(PtP^B) 2850, ²*J*(P^AP^B) 37.5, ³*J*(P^AP^{B'}) 57.5].

This same product was formed by the similar photolysis of $[Pt_2(\mu-H)Me_2(\mu-dppm)_2]|SbF_6]$ (0.03 g) in pyridine (5 mL), but in this case the only gaseous product was CH₄. The product was identified by the ¹H and ⁻³¹P{¹H} nmr spectra.

$[Pt_2Me(Me_2CO)(\mu - dppm)_2][PF_6]$

A solution of $[Pt_2Me_3(\mu-dppm)_2][PF_6]$ (0.05 g, 3.9×10^{-5} mol) in dry acetone (5 mL), in an apparatus with a sidearm fitted with a 1 mm quartz cuvette, was degassed by several freeze-pump-thaw cycles and then photolysed using a 150 W xenon lamp with water and Corning 0-52 filters. The reaction was monitored by uv-visible spectroscopy, and when complete the gaseous phase was analysed by gc. Ethane ($4.0 \pm 0.2 \times 10^{-5}$ mol) was the only gas formed.

The product was isolated as a yellow solid by evaporation of the solvent under high vacuum, and was identified by the ¹H nmr spectrum in (CD₃)₂CO [δ : 0.29, ²J(PtH)70, ³J(PH)7.5, *Me*Pt] and by conversion to [Pt₂Me(C₅H₅N)(μ -dppm)][PF₆] on addition of pyridine. The acetone complex decomposed over a period of several hours to an unidentified product having δ 0.24 [*m*, ²J(PtH)82, ³J(PH)7].

This product 6c, as the SbF₆⁻ salt, was also prepared by similar

photolysis of a degassed solution of $|Pt_2H(\mu-H)Me(\mu-dppm)_2||SbF_6|$ (0.10 g) in (CD₃)₂CO (0.7 mL) and was identified as above.

$[Pt_2Me(CD_3CN)(\mu-dppm)_2][SbF_6]$

This was obtained and identified by photolysis of $[Pt_2H-(\mu-H)Me(\mu-dppm)_2][SbF_6]$ in CD₃CN as described above. ¹Hmr (CD₃CN) δ : 0.80[m, ²J(PtH)60, ³J(PH)6.5 Hz]. This complex was stable in CD₃CN solution in the absence of oxygen, but decomposed on evaporation of the solvent. The same product was formed by similar photolysis of $[Pt_2(\mu-H)Me_2(\mu-dppm)_2][SbF_6]$ or, as the PF₆⁻ salt, by photolysis of $[Pt_2Me_3(\mu-dppm)_2][PF_6]$.

Photolysis of $[Pt_2Me_3(\mu - dppm)_2][PF_6]$ in CD_2Cl_2

 $|Pt_2Me_3(\mu-dppm)_2||PF_6|$ (0.0843 g) was dissolved in CD_2Cl_2 (1 mL) in a 5 mm nmr tube. The solution was then degassed, flame sealed, and then irradiated using a 150 W xenon lamp source filtered through Corning 0-52 and H₂O filters. Photolysis was continued for 30 min. The ¹H and ³¹P{¹H} nmr spectra showed the product to be $|Pt_2Me_2(\mu-Cl)(\mu-dppm)_2||PF_6|$ (29).

The nmr tube was then opened and the gas product analysed by gc. The gases C_2H_6 , CH_4 , and C_2H_4 were observed in a ratio of 1:0.08:0.02. The absolute yield of C_2H_6 was 45% mol/mol 4 decomposed.

$[PtMe(C_5H_5N)(dppm)][NO_3]$

A solution of AgNO₃ (0.060 g) in methanol (12 mL) was added dropwise to a solution of [PtClMe(dppm)] (0.20 g) (29) in CH₂Cl₂ (50 mL). The mixture was then filtered to remove AgCl and pyridine (0.5 mL) was added. After 10 min, the solvent was evaporated under vacuum to give the product. This was characterised by the nmr spectra in C₅D₅N. ³¹Pmr, δ : -26.6[*m*, ²*J*(P^PB)38, ¹*J*(PtP^A)-3388, P^A trans to C₅H₅N], -42.3[*m*, ²*J*(P^PB)38, ¹*J*(PtP^B)1270, P^B trans to Me]. ¹Hmr, δ : 1.02 [*m*, ³*J*(P^BH)8, ³*J*(P^AH)3, ²*J*(PtH)61, *Me*Pt]. These assignments were confirmed by selective ³¹P decoupling experiments.

When the photolysis of $[Pt_2Me_3(\mu-dppm)_2][PF_6]$ was carried out in C_5D_5N with monitoring by ¹H and ³¹P{¹H} nmr, an equimolar mixture of $[PtMe_2(dppm)]$ (29) and $[PtMe(C_5D_5N)(dppm)]^+$ was formed. The parameters for the latter complex were identical with those of the sample prepared above.

Quantum yield determinations

Irradiations were performed with a Jasco CRM-FA Spectroirradiator equipped with a counter. The light flux and counter were calibrated by using ferrioxalate actinometry at 362 ± 7 nm.

In a typical experiment, a solution of $[Pt_2Me_3(\mu-dppm)_2][PF_6]$ in CH₂Cl₂ (4.0 mL, 4.45 × 10⁻⁴ *M*) was degassed by three freeze-pump-thaw cycles, each time pumping to a residual pressure of 5 × 10⁻⁵ mbar at 77 K. The solution was then flame sealed in a 1 cm quartz cuvette. The reaction was monitored by following the change in optical density at 440 nm. The data were then analysed by calculating the concentration of $[Pt_2Me_3(\mu-dppm)_2]^+$ after each irradiation. From this an average concentration over each irradiation interval, and hence the percent light absorbed was calculated. Linear plots of $[Pt_2Me_3(\mu-dppm)_2]^+$ concentration vs. quanta of light absorbed by $[Pt_2Me_3(\mu-dppm)_2]^+$ were obtained (correlation coefficient > 0.99). The quantum yields were then calculated from the slopes of these lines.

The quantum yield measurement in benzene was complicated by precipitation of a white microcrystalline material after $\sim 40\%$ reaction at which stage an isosbestic point at 360 nm was lost. The final absorption was estimated and the quantum yield calculated as 0.6. The error due to this estimation is difficult to assess.

Proof of intramolecular reaction

A mixture of $[Pt_2(\mu-D)(CD_3)_2(\mu-dppm)_2][PF_6]$ (0.025 g) and $[Pt_2(\mu-H)(CH_3)_2(\mu-dppm)_2][PF_6]$ (0.025 g) in pyridine (5 mL) was degassed and photolysed to partial conversion. The gaseous products were analysed using a Varian MAT 311A mass spectrometer. For comparison, photolysis of the pure labelled materials were also carried out and the gases analysed in the same way. The above system gave

 $CD_4:CD_3H:CH_3D:CH_4 = 1:0.04:0.02:1.6.$

Experiments using $[Pt_2(CD_3)_3(\mu-dppm)_2][PF_6]$ and $[Pt_2(CH_3)_3(\mu-dppm)_2][PF_6]$ were earried out in a similar way.

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